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ELECTROKINETIC STUDIES ON COVELLITE, CUPRITE AND TENORITE

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Detailed electrokinetic measurements are conducted on synthetic covellite, cuprite and tenorite particles. The role of potential determining ions identical to that of the particle lattice is considered in addition to usual H^+ and OH^- ions. In the case of CuS, additional charge reversals are noticed between pH $\geq$ 2.5 and $\leq$ 6.0 in addition to the usual charge reversals that occur by direct hydrolysis in the socalled region of metal ion precipitation. Interaction of protons with hydrous mineral surface and the adsorption of desorbed or excess metal ions with protonated surface sites are explained by ion exchange mechanism. Effect of reducing environment and oxidation-reduction reactions on zeta potentials is also discussed.

Key words: Zeta potential, covellite, cuprite and tenorite.

INTRODUCTION

The surface properties of minerals are influenced by the structure of the mineral-water interface and surface reactions such as specific dissolution and adsorption. Many adsorption models have been proposed to justify the chemical complexation reactions occuring at the interface [1–4]. Aqueous surface chemistry of oxides and complex oxide minerals and the principles governing the charging mechanism are well documented by various investigators [5–7].

However, very little attention has been paid to the surface chemistry of sulphide minerals compared to oxide minerals. Among the sulphide minerals, the most extensively studied minerals are sphalerite and galena [8–12]. The chemisorption of water molecules takes place on the metal atoms exposed from the sulphide lattice [13].

$$\equiv MS + H_2O \rightleftharpoons \equiv MSH_2O \qquad (1)$$

Thus the charge neutralization induces proton transfer to neighbouring sulphur atoms and thereby surface functional groups like metal hydroxyl and thiol groups are formed.

$$\equiv MSH_2O \rightleftharpoons \begin{matrix} \equiv MOH \\ \quad SH \end{matrix} \qquad (2)$$

Consequently, two types of surface functional sites namely Brönsted sites (where H^+ and OH^- are potential determining ions) and Lewis acid sites, (where M^{2+} and S^{2-} are potential determining ions) are generated. Recently, amphoteric properties of galena, sphalerite and cadmium sulphide were investigated by potentiometric titrations [13, 14]. These amphoteric properties are ascribed to the presence of CuOH and CuSH binding sites. Several techniques like XPS, potentiometric titrations and zeta potential measurements are widely employed to examine such surface reactions at the mineral-water interface.

In the present investigation, electrokinetic behaviour of synthetic covellite, cuprite and tenorite are studied by zeta potential measurements under the constant ionic strength of 10^{-2} mole l^{-1}. Under the conditions of constant ionic strength of 10^{-2} mole l^{-1} and above, it is generally established that the assumption of zeta potential to be identical to ψ_d is reasonable and accurate except for very long chain polymers [15–17]. It is also accepted to interpret the surface transformations directly by zeta potential measurements [9–11]. In the present study, the role of dissolved metal ions as potential determining ions is examined on the basis of the above statement, i.e. changes in zeta potential will reflect changes in surface potential. These types of measurements have great significance in the flotation of sulphide minerals where substantial quantity of metal ions are dissolved due to oxidation. Simultaneous changes in the concentration of various potential determining ions (PDI) in bulk solution are followed by standard analytical methods along with zeta potential measurements to have a closer look on the role of PDI.

MATERIALS AND METHODS

The characteristics of synthetic covellite cuprite and tenorite used in this investigation are shown in Table I. All the other chemicals used in the experiments are Analar grade.

TABLE-I: Source of minerals and their purity

Material	Surface Area (m^2/g)	Minimum Assay (%)	Maximum impurities (%)	Source
Covellite (CuS)	0.60	98.5	alkali: 1.1 Fe: 0.1	KEBO
Tenorite (CuO)	5.92	99.0	alkali: 0.2 SO_4^{2-}: 0.25	Merck
Cuprite (Cu_2O)	2.15	94.0	CuO: 5.0	BDH

Standard BET method is adopted for surface area measurements. Zeta potential measurements are conducted using Laser Zee meter model 501 in the presence of a constant ionic medium of an indifferent electrolyte (0.1 M $NaClO_4$) prepared in deoxygenated water.

In each experiment, 1.0 g in the case of CuS and 0.1 g in the case of CuO and Cu_2O was taken in a reactor and rinsed several times with 0.1 M $NaClO_4$ electrolyte in argon atmosphere. After rinsing, the particles were allowed to settle and a fixed quantity of supernatant solution was siphoned off. A fresh quantity of electrolyte solution equal to the volume which was siphoned off, is added to the system for continued rinsing. After thorough

$$\equiv CuSH \xrightarrow{+H^+} \equiv CuSH \xrightarrow{+H^+} \equiv CuSH \xrightarrow{+Cu^{2+} + H_2O} \equiv SCuOH \qquad \equiv SCuOH_2^+ \qquad \equiv SH \qquad (5)$$

rinsing, the final volume of the suspension is adjusted to 50 ml and equilibrated for 12 h with a known quantity of 0.1M $HClO_4$ to obtain the starting pH. The pH is adjusted towards alkaline by titrating with known quantity of 0.1 M NaOH. After equilibrating for further 12 h, the final pH is recorded with Corning pH-meter 155 connected to the system. In the case of CuS, the entire operations were conducted under argon atmosphere. After equilibration, the suspension was allowed to settle and a suitable quantity of supernatant solution was siphoned off through a millipore membrane filter (0.22 μm) to estimate the concentration of copper and sulphur species. Copper is quantitatively estimated using atomic absorption spectrophotometer (Pye Unicam SP 1900) and sulphur by Hach radio XR turbidimeter [18]. A few selected samples are analysed for oxysulphur species by ion chromatograph 2010i. Reproducibility is checked by repeated measurements.

RESULTS AND DISCUSSION

Covellite system under argon atmosphere

Initially, when CuS particles are equilibrated with 0.1 M $HClO_4$, depending on the acid concentration, the particles may either slowly dissolve or exhibit ion exchange properties between aqueous protons and surface Cu^{2+} sites at CuS-H_2O interface. The higher concentration of copper ($\approx$ 4 times) compared to the sulphur species shown in Table II supports the desorption of Cu^{+2} from the surface rather than the dissolution process. The Small quantity of sulphur species in bulk solution (Table II) may be due to surface oxidation by residual oxygen by the following reaction:

$$XCuS + 2O_2 \longrightarrow XCu^{2+} + S_XO_4^{2-} \qquad (3)$$

It is to be noted that despite all the conventional efforts to remove O_2 from the system, it is extremely difficult to reduce trace oxygen to an insignificant level. Even without the presence of dissolved oxygen, sulphide ion can be oxidized to sulphate by the incipient oxygen generated from the water oxidation on the very surface of the semiconducting material [19]. Tests conducted to check the possibility of H_2S were found to be negative.

Analysis of the filtrate by ion chromatograph has confirmed that the sulphate is the only sulphur species in all the samples under argon atmosphere. Hence it can be concluded that the copper content in the solution is solely due to interaction of protons with hydrous CuS surface desorbing Cu^{2+} ions from the surface by the following mechanism:

$$\equiv CuS \xrightarrow{+H_2O} \equiv CuSH \qquad \equiv SCu \qquad \equiv SCuOH \qquad (4)$$

Thus the charge neutralization and subsequent interaction of H+ ions with hydroxylated metal atoms will lead to metal deficient surface. The interaction of protons with hydrous CuS surface involves the desorption of Cu^{2+} ions.

Figure 1 shows the changes in zeta potentials with pH under argon atmosphere. Negative zeta potential values observed at low pH levels indicate metal deficient surfaces like S and SH. On gradual addition on OH^- to such suspension, the protons will be neutralised and released. Consequently, bare Cu^{2+} from solution will diffuse and occupy Lewis acid sites by ion exchange process. Thus, the first charge reversal CR(I) from −ve to +ve can be

TABLE-II: Changes in the concentrations of copper and sulphur at various pH values

NaOH (0.1M) added (ml)	Under Argon Gas Bubbling: pH of suspension	Concentration (mM) Cu^{2+}	Concentration (mM) SO_4^{2-}	In the absence of argon: pH of suspension	Concentration (mM) Cu^{2+}	Concentration (mM) Total S
0.0	2.49	1.65	0.43	5.37	0.35	0.21
0.1	2.54	1.51	0.38	5.58	0.34	0.09
0.3	2.56	1.32	0.35	5.35	0.32	0.26
0.6	2.62	1.31	0.34	5.66	0.30	0.56
1.0	2.89	1.30	0.34	5.82	0.26	0.00
1.5	3.70	1.21	0.40	6.21	0.24	0.00
2.0	4.60	0.92	0.40	–	–	
2.5	6.43	0.50	0.09	6.38	0.15	0.00
3.0	6.85	0.18	0.10	–	–	–
3.5	9.94	0.00	0.55	6.58	0.09	0.00
4.5	11.76	0.00	0.76	–	–	–
4.7	–	–	–	7.22	0.00	0.00
5.1	–	–	–	7.50	0.00	0.21
10.0	–	–	–	11.85	0.00	2.81

explained as due to adsorption of Cu^{2+} on the surface according to the following equation

$$\equiv CuSH \qquad \equiv CuS-Cu^+ + H^+$$
$$\equiv SH + 3\,Cu^{2+} \longrightarrow \equiv S-Cu^+ + H^+ \qquad (6)$$
$$\equiv S^- \qquad \equiv S-Cu^+$$

Recent investigations on galena and sphalerite demonstrated such ion exchange process between aqueous protons and surface metal sites and vice versa [14]. The concentration of copper and sulphur in the bulk was measured together with pH and zeta potential measurements. The results of the same are presented in Table II. The decrease in the concentration of Cu^{2+} with a small shift in pH is in agreement with ion exchange mechanism. The abstraction of metal ions from bulk solution to their original positions on the surface (surface doping) was discussed [20]. In the surface doping process, the coordination sites exposed to the complexation are restricted compared to that of metallic sites exposed from the surface.

The further charge reversal from positive to negative at pH 5.5 is due to the reduction of Cu^{2+} to Cu^+ with a simultaneous oxidation of sulphur.

$$\equiv CuS - Cu^+ + e \longrightarrow \equiv Cu_2S \qquad (7)$$

The simultaneous oxidation of sulphur either from the neighbouring SH sites or from CuS sites is a complementary process for the above reduction of copper. At this juncture, it is worth recalling some earlier investigations on the activation of sphalerite by Cu^{2+}. Many of the investigators have suggested the formation of Cu_2S on an activated surface by various updated surface studying techniques like XPS, SAM, SEM and cyclic

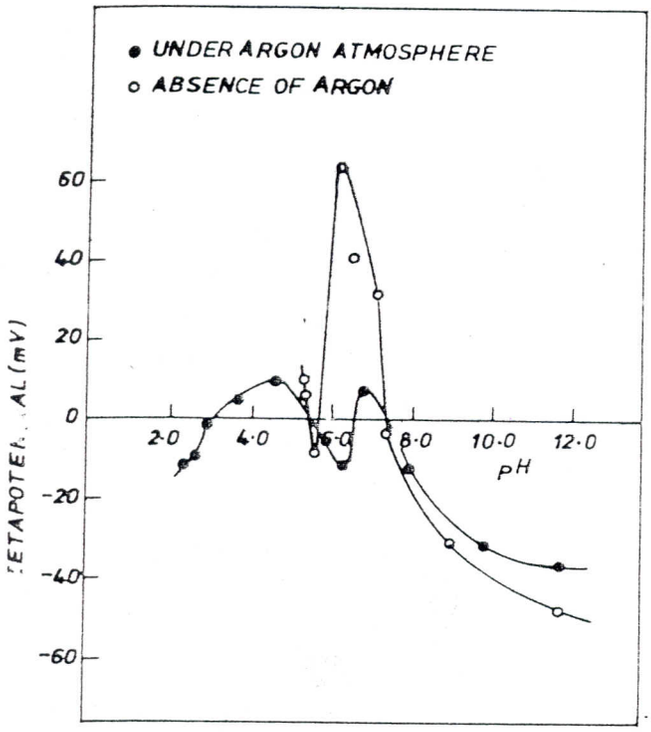

Fig. 1: Zeta potential of CuS in the presence and absence of argon atmosphere.

voltametry [21, 22]. In the case of covellite, self redox reactions such as

$$2CuS \longrightarrow Cu_2S + \dot{S} \quad (8)$$

$$CuS \longrightarrow Cu^{2+} + \dot{S} + 2e \quad (9)$$

$$2Cu^{2+} + e^- \longrightarrow Cu^+ \quad (10)$$

are possible which lead to the formation of Cu^2S.

Finkelstein and Allison [23] have indicated that rearrangement of lattice may occur causing a distorted structure composed of upric and cuprous sulphide formed by redox reactions. The Cu_2S thus formed, in turn, exhibit a pH dependent adsorption behaviour against the dissolved Cu^{2+} ions.

The third charge reversal CR(3) from negative to positive at a pH of around 6.5 is due to the onset of adsorption of copper hydroxy species like $CuOH^+$ with positive charge. Further charge reversal CR(4) from positive to negative at a pH of around 8.0 corresponds to the point of zero charge of $Cu(OH)_2$ precipitate. CR(4) reflects the properties of partial or complete coating of copper hydroxide on the surface. As the hydroxyl-coating coating approaches full coverage, the values of CR(4) approaches the actual PZC of copper hydroxide colloid itself. The surface precipitation mechanism has been interpreted in different ways [24, 25].

CuS system in the absence of argon atmosphere:

Similar set of experiments were conducted in the absence of argon atmosphere. When 3.0 ml of 0.1 m $HClO_4$ was added to the suspension, the initial pH was found to be 2.47. However, after equilibration for 12 h the pH was shifted to 5.37 (Table II). This shift in pH is totally different from the similar experiment, conducted under argon atmosphere. The shift in pH from an initial value of 2.47 to 5.37 can be explained as due to the simultaneous oxidation of sulphur and reduction of oxygen by consuming free protons available in the suspension.

$$\frac{1}{2} O_2 + 2H^+ + S^{2-} \longrightarrow H_2O + \dot{S} \quad (11)$$

The pH of the suspension was adjusted to alkaline region by titrating it with 0.1N NaOH. While there was a gradual increase in pH in the presence of argon atmosphere, fluctuations in pH are noticed in the absence of argon atmosphere. Initially, when the suspension was back titrated with NaOH, the pH was found to shift slightly towards the acidic region. The drift in the pH region accompanied by a shift in zeta potential from positive to negative and an increase in sulphur content in bulk solution support the formation of Cu_2S according to the following surface reaction.

$$\not{2}CuS - Cu^+ + SH^- \longrightarrow \not{2}Cu_2S + \dot{S} + H^+ \quad (12)$$

In the absence of argon atmosphere the major portion of sulphur in the bulk solution is found to be in form of elemental sulphur. The only oxysulphur species varying between 0.01 mm and 0.2 mm is SO_4^{2-}. Therefore, in the presence of traces of oxygen it is difficult to assess the exact role of dissolved species on zeta potential, since other parallel reactions like reduction of oxygen, copper and oxidation of sulphur occur both in the bulk phase and at the surface. Thus the presence of oxygen arising out of contamination may have an overriding influence on surface oxidation reactions.

In the absence of argon atmosphere, a steep increase in zeta potential followed by a sudden decrease indicates high adsorption of metal hydroxy species in the region of precipitation. In fact, results shown in Table II indicate such high abstraction of copper from bulk solution.

Figure 2 shows the effect of additional Cu^{2+} (copper perchlorate) and S^{2-} (sodium sulphide) on zeta potential. Though the general trend of the curves remained almost the same as in Fig. 1, the adsorption of Cu^{2+} and the magnitude of zeta potential remained constant in the region of ion exchange even in the presence of excess Cu^{2+}. It was also noticed that the CR(3) shifted to higher pH whereas CR(4) shifted to lower pH as the concentration of metal ion decreased. These observations are in accordance with the pH dependence of metal hydroxide precipitation with metal ion concentration in bulk solution as suggested by James and Healy [25]. This has been further illustrated by equilibrium diagrams corresponding to 10^{-3}, 10^{-4} and 10^{-5}M Cu(II) solutions (Fig. 3). The following stability constants from Martel and Smith [26] were used for the above calculations.

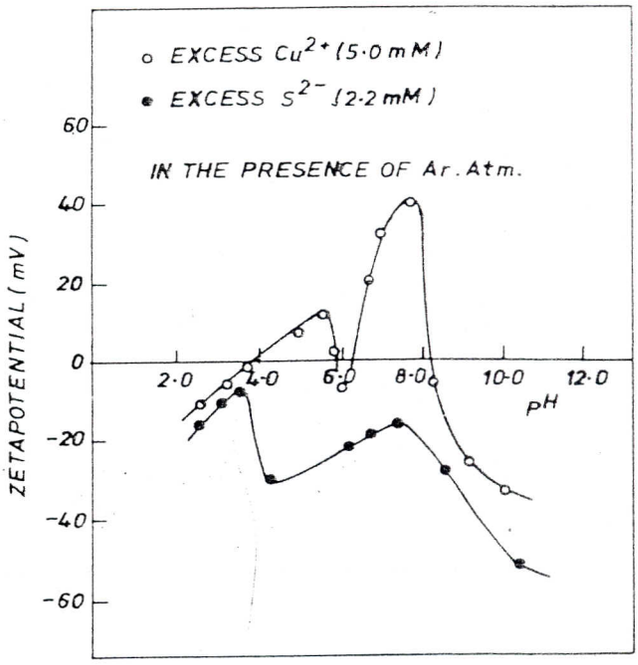

Fig. 2: Zeta potential of CuS in the presence of excess Cu^{2+}.

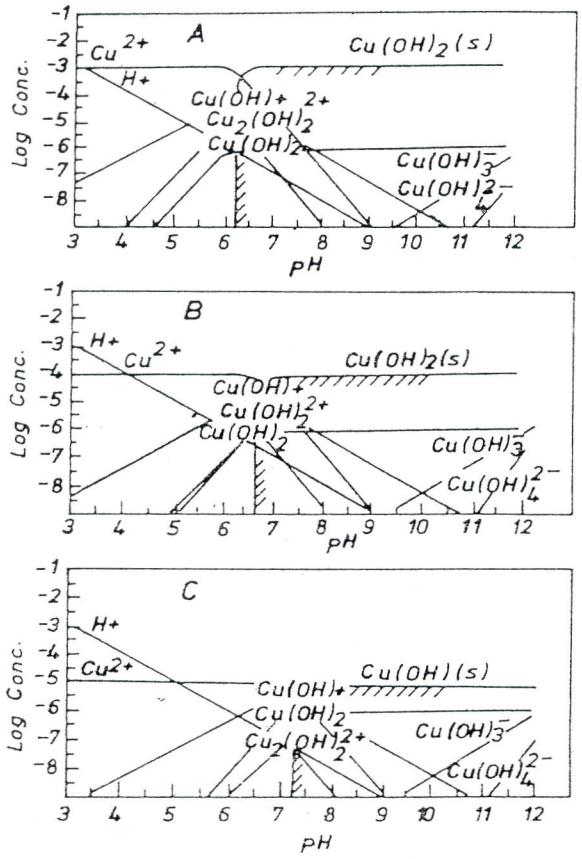

Fig. 3: Species distribution diagram for Cu(II) (A) 10^{-3}M, (B) 10^{-4}M and (C) 10^{-5}M solutions.

				Log K
Cu^{2+}	+ OH^-	═══	$Cu(OH)^+$	6.6
$2Cu^{2+}$	+ $2OH^-$	═══	$Cu_2(OH)_2^{2+}$	17.0
Cu^{2+}	+ $3OH^-$	═══	$Cu(OH)_3^-$	14.5
Cu^{2+}	+ $4OH^-$	═══	$Cu(OH)_4^{2-}$	15.6
Cu^{2+}	+ $2OH^-$	═══	$Cu(OH)_2$ (aq)	12.8
Cu^{2+}	+ $2OH^-$	═══	$Cu(OH)_2$(S)	19.3

These diagrams illustrate the precipitation edge of $Cu(OH)_2$(S) increasing with pH from 6.2 to 7.3 as the Cu(II) concentration decreases.

Figure 2 suggests that even in the presence of reducing environment, Cu^{2+} can act as PDI by replacing H^+ from surface SH sites. The reduction of copper ions (formation of Cu_2S) has been attributed to lowering of pH values caused by the reducing environment (Na_2S) on the surface. Species distribution diagram of copper sulphides using Sol gas water program suggests such a shift caused by enhancing the reducing environment. Though the zeta potentials were negative, surface variations continued to be similar. Sulphide species can indirectly affect the surface by reducing surface copper ions. However, from the experiments conducted, it is rather difficult to assess the potential determining role of sulphide ions since free S^{2-} can exist only in very high alkaline pH. Further, excess sulphide ion at low pH (< 6.0) imply further precipitation of Cu_2S.

Copper Oxide Minerals

In the case of oxide minerals, charge can develop on a hydroxylated surface through amphoteric dissociation of surface –OH groups. Accordingly, acid dissociation produces negative surface sites and basic dissociation produces positive surface sites.

$$\equiv MOH \rightleftharpoons \equiv MO^- + H^+ \quad (13)$$

$$\equiv MOH \rightleftharpoons \equiv M^+ + OH^- \quad (14)$$

$$\equiv MOH_2^+ \rightleftharpoons \equiv MOH + H^+ \quad (15)$$

In the presence of dissolved or excess metal ions, protons liberated via acid dissociation are expected to exchange with bulk metal ions.

Variations in zeta potentials with pH at Cu_2O-H_2O and $CuO-H_2O$ interfaces are shown in Figs. 4 and 5. When suspension is titrated with hydroxyl ions, the initial change in zeta potentials is towards more positive values. This can be attributed to adsorption of bare Cu^{2+} from the bulk phase. Because of the high solubility of copper oxides compared to copper sulphides, zeta potentials were measured from pH 5.50 onwards.

$$\equiv CuOH \rightleftharpoons \equiv CuO^- + H^+_{aq} \quad (16)$$

$$\equiv CuO^- + Cu^{2+} \rightleftharpoons \equiv CuO - Cu^+ \quad (17)$$

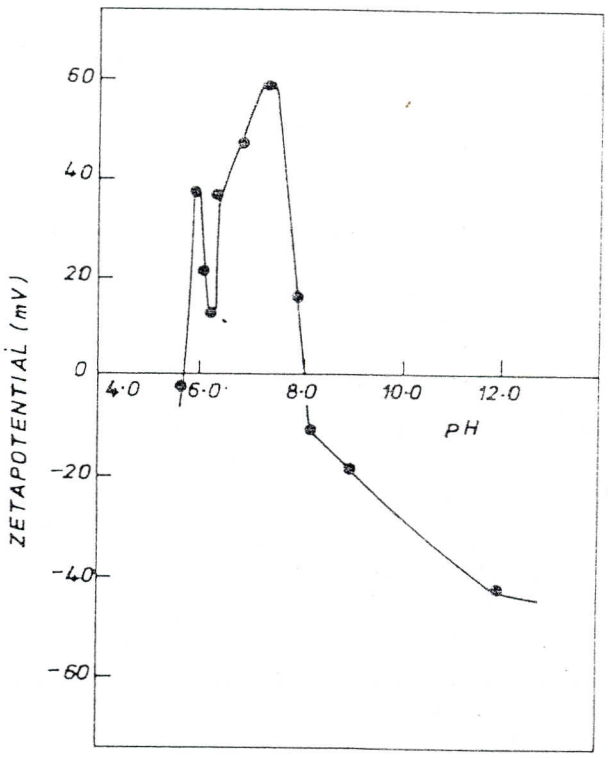

Fig. 4: Zeta potential of cuprite as a function of pH.

The overall process can be visualised as ion exchange between protons from surface and metal ions from bulk solution. Copper atoms coordinated to the surface are hydroxylated by further addition of OH^-. It has been shown that the precipitation reactions which occur in the interfacial region are controlled by the activities of the species in the bulk solution [25]. The sudden drop in zeta potentials from positive to less positive or neutral can be visualised according to the following surface reaction:

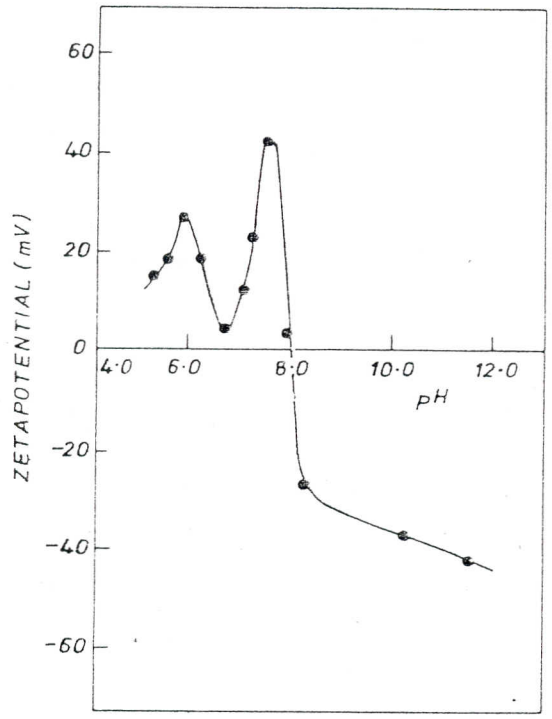

Fig. 5: Zeta potential of tenorite as a function of pH.

$$\text{CuO}-\text{Cu}^{+} \qquad \text{CuO}-\text{CuOH}$$
$$+ \ \text{OH}^{-} \ \rightleftharpoons \qquad (18)$$
$$\text{CuOH} \qquad \text{CuOH}$$

Though the species like $(CuOH)^+$ are simultaneously formed in the bulk, the adsorption of the same was obstructed due to electrostatic repulsion between positively charged surface and $(CuOH)^+$. The onset of adsorption of $(CuOH)^+$ species from the bulk may start only after considerable decrease in positive zeta potential. Since the entire change occurs within a narrow pH range, close readings are essential to notice such shift in zeta potential.

Changes in zeta potential above pH 6.0 are related to adsorption of copper hydroxy species similar to that of precipitation. Calculated PZC value (pH = 8.01) for $Cu(OH)_2$ was found to be in good agreement with experimental PZC value (pH = 8.00).

Since the copper ions (Cu^+) dissolved from Cu_2O are highly unstable and disproportionate in water, it is obvious that the dissolved metal ions are in the form of Cu^{2+}. Hence the copper ion species adsorbed on Cu_2O can be inferred as Cu^{2+}.

CONCLUSIONS

Detailed electrokinetic measurements conducted on synthetic covellite, cuprite and tenorite have shown that by careful control of experimental parameters, much new information on mineral-water interface can be obtained. In addition to H^+ and OH^- ions, ions that are identical to surface lattice ions are found to play a dominent role as potential determining ions. The results demonstrate ion exchange process between surface protons and aqueous metal ions and vice versa in the pH region 2.5–6.0. Consequently, additional charge reversals besides charge reversals in the region of metal ion precipitation are newly noticed by us. These results suggest that sulphide minerals may possess two distinct regions of charge reversals, namely, ion exchange region between dissolved metal ions and surface protons and the region of metal hydroxide precipitation. Formation of metal deficient/sulphur rich surfaces may be responsible for such additional charge reversals. In a way, surface changes that can be quantified by potentiometric titrations can be visualized qualitatively through zeta potential measurements. Role of sulphide ion at the interface was found to be less pronounced compared to that of Cu^{2+}. The sulphide ion may indirectly affect the surface by involving in the reduction of CuS to Cu_2S.

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